Journal of Non-Crystalline Solids 362 (2013) 69–72

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Interstitial-oxygen induced localized vibrational properties in alpha-quartz

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ARTICLE INFO

Article history:
Received 20 September 2012
Received in revised form 21 November 2012
Available online 23 December 2012

Keywords:
Quartz;
Oxygen interstitials;
Defect structure;
Localized vibrations

ABSTRACT

Local configurations and localized vibrations of oxygen interstitials in different charged states in alpha-quartz are investigated by computer calculations. First-principle potentials of the Buckingham type have been used in numerical modeling. The study of the lattice dynamics in defective crystal is performed using the phonon local density of states. Frequencies of localized vibrations induced by oxygen interstitials are determined. It is shown that the atomic configuration, type, number and frequency of localized vibrations depend on the sign and magnitude of the interstitial atom charge.

1. Introduction

Silicon dioxide can exist in numerous crystalline and amorphous forms and has a variety of technological applications [1] due to its unique electric, optical, piezoelectric and mechanical characteristics. Here we focus on the structural and lattice-dynamical properties of the low-temperature phase of silicon dioxide (alpha-quartz), which belong to the trigonal crystal system and is described by one of the space enantiomorphic symmetry groups $P3_121$ (left-handed form) or $P3_221$ (right-handed form). Investigations of these properties have a long history. The atomic structure and vibrational properties of perfect alpha-quartz have been the subject of extensive and productive studies, both experimental [2–5] and theoretical [6–10].

Many of peculiar characteristics of α-SiO_2 depend crucially on the point defects and their concentration. The important intrinsic defects in alpha-quartz are oxygen vacancies and interstitials that may exist in several charge states [11]. The description of dynamic processes occurring with participation of these defects requires information about localized vibrations induced by defects. In many cases this information can be obtained only from numerical simulations. While there are several works [12,13] specifically addressed to measure the impact of oxygen vacancies on the phonon spectrum of alpha-quartz, the effect of oxygen interstitials has not been thoroughly examined.

The present paper is devoted to the investigation of the local configurations and the vibrational properties of alpha-quartz containing oxygen interstitials. These defects may appear in four charged states: O^{-2}, O^{-1}, O^{0} and O^{+1}. In this study we present the computer simulation results which allowed to evaluate the effect of oxygen interstitials on the structure and the phonon spectrum of α-SiO_2.

2. Calculation methods

The simulation of both atomic configurations and lattice dynamics in SiO_2 containing charged defects encounters considerable difficulties. It is necessary to consider slowly decreasing Coulomb interactions. The cluster technique allows a correct description of long-range electrostatic interactions that was shown by us earlier [14].

In this approach, the crystal with a defect is divided into several spherical regions: an inner region 1 and an outer region 2 + 3, as shown in Fig. 1. The region 1 is surrounded by the finite region 2. These regions are treated atomistically. The region 3 is represented in the approximation of continuum. Atom displacements in region 1 can be determined by direct minimization of the static lattice energy in the context of the work [15]. Atoms in the region 2 are kept fixed in their ideal positions.

The interactions between atoms were described by the ion model [16]. The interionic potential U_{ik} of the force field is a function of the positions of i and k ions and has three components (repulsion, van der Waals and Coulomb, respectively):

$$U_{ik} = U(r_{ik}) = A_{ik}\exp(-r_{ik}/\rho_{ik}) - \frac{C_{ik}}{r_{ik}^6} + \frac{Z_i Z_k}{r_{ik}}. \quad (1)$$

Here $r_{ik} = |r_k - r_i|$ is the distance between ions i and k; Z_i is the effective charge of the ion i; A_{ik}, ρ_{ik} and C_{ik} are the parameters. The numerical values of parameters appeared in Eq. (1) are used which have been presented in [16]. They derived from *ab initio* calculations.

The effect of oxygen impurities on the vibration spectrum of α-quartz was studied by calculating the phonon local densities of states (LDOS) in the perfect and defective crystals. The LDOS at the

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http://dx.doi.org/10.1016/j.jnoncrysol.2012.11.031

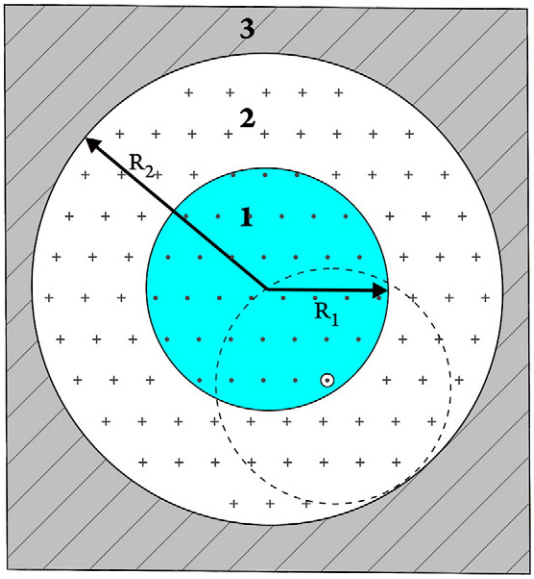

Fig. 1. The structural model of a cluster for crystal lattice structure calculations.

site of *i*-th ion in the α-th Cartesian direction is calculated using the expression: [17]

$$G^i_\alpha(\omega) = -\frac{2\omega}{\pi} Img_\alpha(i,\omega), \tag{2}$$

where $g_\alpha(i,\omega)$ are diagonal elements of the Fourier transform of the retarded Green function, which are determined by the relationship: [18]

$$g_\alpha(i,\omega) = \langle i\alpha| \frac{I}{I(\omega^2 + i0) - D} |i\alpha\rangle. \tag{3}$$

Here I is the unit matrix, D is the dynamic matrix of the cluster and the vector $|i\alpha\rangle$ has the dimensionality 3 N (N being the number of ions in the cluster).

The Lanczos recursion [19] has been applied to the calculation of the LDOS. The Lanczos algorithm is a technique to transform a dynamic matrix D into an equivalent tridiagonal form. Detailed expressions were presented in Ref. [20].

3. Results

At the initial stage of modeling we have calculated the equilibrium structure of the perfect crystal using the *ab initio* pair interionic potentials [16] for α-SiO_2. The obtained values of the lattice constants are $a = 4.95$ (4.91) Å and $c = 5.46$ (5.41) Å, where the numbers in parentheses are the experimental values [21] at 300 K. The corresponding experimental values are found to be slightly less. It is well known that a hexagonal elementary cell consists of three slightly distorted silicon-oxygen SiO_4-tetrahedrons that are connected through a common oxygen ion. In these tetrahedrons the Si – O bonds for two oxygen ions are 1.598 Å long, while the other two are 1.606 Å long. Any oxygen ion forms only two O – Si bonds of different lengths. These values are also in agreement with the data reported in [21], although the bond lengths are slightly larger than the experimental values: 1.606 Å and 1.614 Å.

Then the optimized structure was used for calculations of alpha-quartz phonon spectra, namely the dispersion curves in highly symmetric directions ([100], [010] and [001]) of the Brillouin zone and the density of states (DOS). It should be noted that detailed discussion of these calculated results was presented in our work [13]. We only emphasize that a cluster with inner region 1 radius of 18.2 Å containing 2000 ions and with region 2 containing nearly 3200 ions in which the Lanczos technique is used to 10–12 levels of recursion is sufficient to reproduce the phonon DOS. This is proved by the comparison of the calculated results and experimental data. It was shown that the phonon DOS consist of two frequency bands and a large forbidden band. The upper boundary of the first-frequency band is 28.2 (24.9) THz, the high-frequency band extends from 32.4 (32.2) to 37.6 (37.4) THz, where the experimental measurements [4] are shown in parentheses for comparison. The Lanczos recursive method allows studying the lattice dynamics for both perfect and defective crystals.

At the next step of the computer simulation the new positions of the ions were determined in the presence of oxygen interstitials. There are structural voids between SiO_4-tetrahedrons in the perfect alpha-quartz crystal lattice. We have selected one of the voids and place the coordinate system origin at its center. Nearest two oxygen ions in regular positions are located at a distance of 1.978 Å from the void center. Subsequently, one of these ions will be denoted by O(1). Two silicon ions situated at distances of 2.305 Å and 2.645 Å from the coordinate origin are denoted as Si(1) and Si(2), respectively. This virginal configuration is shown in Fig. 2. Oxygen interstitial species were placed in the center of the void. Distortions of the crystal lattice were obtained by the potential energy minimization of interstitial-containing α-SiO_2. These relaxed configurations are also shown in

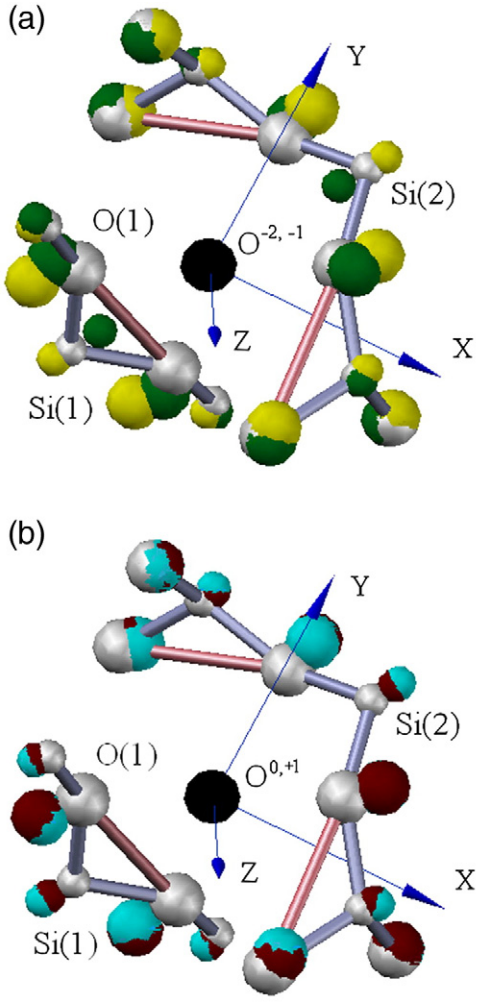

Fig. 2. Structural fragments of perfect and defective α-quartz with oxygen interstitials O^{-2} or O^{-1} (a), O^0 or O^{+1} (b). The atoms before the lattice relaxation are marked gray color; atoms after the relaxation for different oxygen interstitials: green (O^{-2}), yellow (O^{-1}), brown (O^0) and blue (O^{+1}).

Fig. 2. The distances between the positions of interstitials and some nearest ions (O, Si) in the relaxed configurations are reported in Table 1.

The final modeling phase consists of the phonon LDOS calculation for all the ions located within a sphere of 3.2 Å radius around oxygen interstitials in a defective crystal or around the position in which an oxygen interstitial should occur in a perfect crystal. Specific features of the LDOS in a defective crystal, which differ from those of the LDOS in a perfect crystal, corresponded to the localized vibrations (resonant, gap and local) induced by the interstitial. For example, phonon LDOS projected on the displacements of oxygen interstitials are presented in Fig. 3 and phonon LDOS projected on the O(1)-displacements in perfect and in crystals with interstitial O^{+1} are shown in Fig. 4. According to Fig. 4 the O^{+1} interstitial induces a 18.8 THz resonant vibration, 31.2 THz gap vibration and a 38.4 THz localized vibrations on the O(1) ion. The frequencies of localized vibrations in α-quartz induced by oxygen interstitials in different charged states are listed in Table 2.

4. Discussion

The authors are unaware of any experimental studies of the lattice structure and dynamics for atomic oxygen interstitials. The only theoretical work [11] investigates the structure of alpha-quartz containing oxygen interstitials by means of density functional theory. Our calculations allowed us to perform a comprehensive analysis of the lattice relaxation around oxygen interstitials in different charged states and to show that these defects induce strong anisotropic lattice distortions. One can see from the Table 1 and Fig. 2 that the character of the lattice relaxation strongly depends on the charge state of the oxygen interstitial.

During the formation of the oxygen interstitials the ions surrounding these defects are displaced to new equilibrium positions. For the negatively charged oxygen interstitial O^{-2} we have found possible local configuration, which is shown in Fig. 2(a). The calculations predict a displacement of the Si(1) and Si(2) ions to the O^{-2} interstitial. The distances between O^{-2} interstitial and the Si(1) and Si(2) ions are equal to 1.806 Å and 2.165 Å, respectively. These distances are much shorter than the distances between the center of the void and the Si(1) and Si(2) ions in a perfect lattice (2.305 Å and 2.645 Å). The oxygen ion O(1) is placed away from the oxygen O^{-2} interstitial. The distance between interstitial O^{-2} and the O(1) equals to 2.328 Å that is significantly more than the distance of 1.978 Å between the center of the void, and the O(1) in undistorted lattice. The displacement character estimated for the Si(1) and Si(2) ions occurring with the O^{-1}, O^{0} and O^{+1} ion introductions considerably differs from the case of O^{-2}. The shifts of silicon ions are directed away from the defects. The more positive becomes the charge of interstitials, the larger become the Si(1) and Si(2) displacements.

The oxygen interstitials introduce considerable changes in the phonon spectra of the alpha-quartz. The phonon LDOS projected on the displacement directions of oxygen interstitials significantly differs from the LDOS projected on the O(1)-displacements in perfect and in defect crystals (see Figs. 3 and 4). It is worth of note that the oxygen interstitials (O^{-2}, O^{-1}, O^{0} and O^{+1}) do not contribute to the high-frequency vibrations, as there is no high-energy band in the calculated LDOS. One can observe the following regularity during the change of interstitial oxygen charge state. A shift of local phonon density to the low-frequency range occurs when the oxygen interstitial charge state changes from −1 to +1. The shift is caused by the decrease of corresponding effective force interaction for the interstitial.

Table 1
Distance (Å) between oxygen interstitial and nearest ions.

Ion	Charge of interstitial			
	−2	−1	0	+1
O(1)	2.328	2.602	2.565	2.530
Si(1)	1.806	2.565	2.725	2.821
Si(2)	2.165	2.938	3.037	3.101

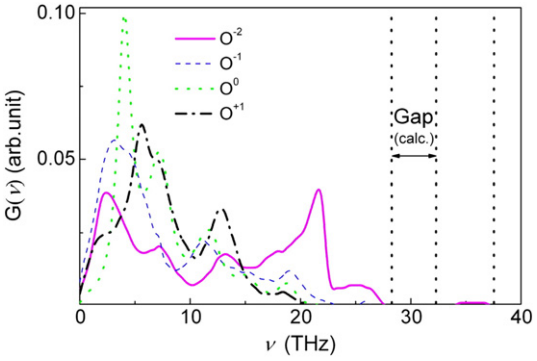

Fig. 3. Phonon LDOS is projected on the displacements of oxygen interstitials.

The O^{-2} interstitial induces five localized vibrations at the nearest ions. Four of them are resonant with corresponding frequencies of 3.2 THz, 13.2 THz, 14.4 THz and 20.8 THz while the rest one is a 29.2 THz gap vibration (see Table 2). The recursive method used allows to estimate the contribution of the ion vibrations in the formation of the localized mode. For instance the O(1) and Si(1), Si(2) ions are involved significantly in the formation of a 13.2 THz resonance vibration (see Table 2). One may also notice that the gap vibration of 29.2 THz is caused by the motion of O(1) ion.

Besides the resonant and gap vibrations the O^{-1}, O^{0} and O^{+1} interstitial ions also induce localized vibrations at the nearest atoms. The frequency of local vibrations is close to the upper-frequency boundary of the optical band. Let's consider the case of O^{-1} ion. According to the calculations, this defect induces one local, two gaps and three resonant vibrations. One of the gap vibrations is connected to the movement of silicon atom Si(2) and has a frequency near the low-energy border of the forbidden band. Other gap vibration with a frequency situated in the middle part of the forbidden band is caused by the movement of oxygen atom O(1). Contrary to gap and local vibrations, the resonant vibrations have frequencies in a low-energy optical band of spectrum.

Considering the data of Table 2 one may see the following regularity: the change of interstitial oxygen charge state from −1 to +1 leads to the slight decrease of the gap vibrations frequencies, while the localized vibration frequencies demonstrate a minor increase. Thus it can be stated that the presence of interstitial oxygen within the alpha-quartz lattice induces substantial distortions of the local atomic structure in the nearest neighborhood and forms the vibrational spectra creating the localized vibrations of different types.

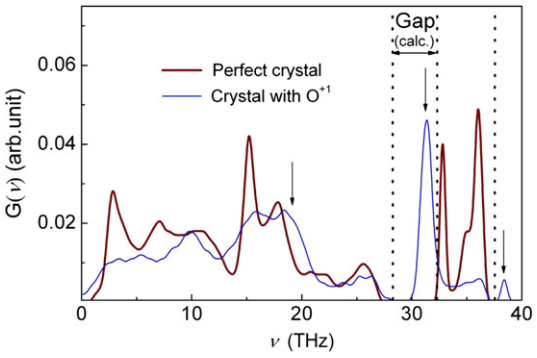

Fig. 4. Phonon LDOS is projected on the O(1)-displacements in perfect α-SiO_2 and in crystals with interstitial O^{+1}. Arrows mark the localized vibrations that involve O(1).

Table 2
Frequencies (THz) of localized vibrations induced by oxygen interstitials on nearest ions.

Interstitial	Ion	Resonant vibrations	Gap vibrations	Local vibrations
O^{-2}	O(1)	13.2, 20.8	29.2	
	Si(1)	3.2, 13.2, 14.4, 20.8		
	Si(2)	3.2, 13.2, 20.8		
O^{-1}	O(1)	19.6	32.4	37.6
	Si(1)	16.8	30.8	37.6
	Si(2)	3.2, 19.6		37.6
O^{-0}	O(1)	19.2	32.4	38.0
	Si(1)	10.4, 14.8, 27.2	30.4	38.0
	Si(2)	7.2, 19.2		38.0
O^{+1}	O(1)	18.8	31.2	38.4
	Si(1)	2.4, 26.8	31.2	38.4
	Si(2)	5.6, 18.8	29.6	38.4

5. Conclusion

In this work we have performed modeling the static lattice distortions and the lattice dynamics in the α-quartz crystal with oxygen interstitial species in different charged states. The effect of oxygen interstitials on the local atomic structure and the vibration spectrum was studied taking a cluster of 2000 ions and using first-principle potentials of the Buckingham type were determined.

We found that the change in the charge state of the defect has a greater impact on the distance between interstitial atom and nearest silicon atoms, but it does not strongly affect onto distance to the nearest oxygen atoms. Our calculations have allowed to determine the frequencies of localized vibrations induced by differently charged oxygen interstitials as well as to evaluate the role of different ions in the formation of defect vibrations. Only resonant and gap vibrations are induced in alpha-quartz due to presence of O^{-2} interstitial whereas the O^{-1}, O^{0} and O^{+1} defects are creating additionally the local variations.

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